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Hawley's Condensed Chemical Dictionary

ELEVENTH EDITION

Revised by

N. Irving Sax
and
Richard J. Lewis, Sr.



VAN NOSTRAND REINHOLD
New York

f dark minerals with a stream beds and on lmenite are usually pres- 1 other minerals.

hosphate).

ion of β -oxoesters by rboxylic esters with zinc s. The intermediate or- cts with the nitrile and ed with 30% potassium

reaction. Introduction aromatic rings on treat- and hydrochloric acid chloride.

2. Cyclization of dicar- with acetic anhydride ydrides or ketones de- ve positions of the car- 1,5-diacids give anhy- which the carboxy groups moved positions give ke-

arium sulfate.

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anionic dispersing agent m salt of a sulfonated 90% active.

igments, earths, and agent in insecticide for- industry for slime con- tion of pitch, reducing ve sizing, etc.; in the ching, dispersing, level- nt.

optical whitening derivative used as whit- lon, acetate rayon, and ls. Stilbene derivatives cotton and rayon fab- hold and industrial de-

"Blandol."⁴⁵ TM for white mineral oil (NF).

Use: Pharmaceutical and cosmetic formulations, plasticizers, paper penetrants, foam depressants.

blank. (1) A piece of material of any desired shape cut by a stamping die prepared for further processing. (2) See control (1).

blast furnace. A vertical coke-fired furnace used for smelting metallic ores, e.g., iron ore.

blast-furnace gas. Byproduct gas from smelting iron ore obtained by the passage of hot air over the coke in the blast furnaces. A typical gas will analyze 12.9% carbon dioxide, 26.3% carbon monoxide, 3.7% hydrogen, 57.1% nitrogen.

Hazard: Toxic by inhalation. See carbon monoxide.

Use: Heating blast-furnace stoves, boiler, or gas-engine fuel.

blasting agent. See black powder; ammonium nitrate; explosive, high, permissible, and low.

blasting gelatin. (SNG). A type of gelatinized dynamite containing approximately 7% of nitrocellulose.

Hazard: High explosive.

blasting powder. See black powder.

"B-L-E."²⁴⁸ TM for high-temperature reaction product of diphenylamine and acetone.

Properties: Dark-brown, viscous liquid; d 1.087; soluble in acetone, benzene, and ethylene dichloride; insoluble in gasoline and water. Combustible.

Use: General-purpose rubber antioxidant.

bleach. To whiten a textile or paper by chemical action. Also the agent itself. Bleaching agents include hydrogen peroxide (the most common), sodium hypochlorite, sodium peroxide, sodium chlorite, calcium hypochlorite, hypochlorous acid, and many organic chlorine derivatives. Chlorinated lime is a bleaching powder used on an industrial scale. Household bleaching powders are sodium perborate and dichlorodimethylhydantoin.

Hazard: See calcium hypochlorite; lime, chlorinated. Some bleaching agents are toxic and strong oxidizing agents.

bleaching assistant. A material added to bleaching baths to secure more rapid and complete penetration of the bleach or improved regulation of the bleaching action, e.g., compounds of sulfonated oils and solvents, soluble pine oils, fatty alcohol salts, sodium silicate, sodium phosphate, magnesium sulfate, and borax.

bleach liquor. A solution of calcium hypochlorite and water.

bleed. (1) When a dye runs. (2) To release pressure gradually as via a valve.

blend. A uniform combination of two or more materials either of which could be used alone for the same purpose as the blend. For example, a fabric may be a blend of wool and nylon either of which is itself usable as fabric. Instances of materials that are often blended are:

plastics (polyblends)	grains
whiskeys	coffees
fabrics	paints
colors	tobaccos
metal powders	solvents
fertilizers	

See also mixture, mixing, kneading.

"Blendex."⁵²⁵ TM for synthetic resinous products prepared from a variety of copolymer combinations. They are used to modify other polymers to attain a wide range of properties.

bleomycin. A glycopeptide antibiotic produced by *Streptomyces verticillus*, it functions as an anti-neoplastic and diagnostic agent. The molecule is exceedingly complex, but synthesis was achieved in 1982. It is a colorless to yellowish powder, soluble in water and methanol but insoluble in acetone and ether. It induces rupture of DNA strands.

blinding. (blister copper).

Properties: Copper (96-99% purity) produced by the reduction and smelting of copper ores. It has a blistered appearance probably caused by gas pockets. It is usually further refined electrolytically.

blister gas. See dibromodiethylsulfide.

blister packaging. A type of packaging used widely in the food and pharmaceutical industries consisting of a hollow cavity of various shapes and capacities in which the material is enclosed. Polyester and polyethylene resins are often used.

block. (1) Undesirable cohesion of films or layers of plastic.

See antiblock agent.

(2) A type of polymer.

See block polymer.

block polymer. A high polymer whose molecule is made up of alternating sections of one chemical composition separated by sections of a different

chemical nature or by a coupling group of low molecular weight. An example might be blocks of polyvinyl chloride interspersed with blocks of polyvinyl acetate. Such polymer combinations are made synthetically. They depend on the presence of an active site on the polymer chain which initiates the necessary reactions.

See also graft polymer, stereoblock polymer.



blood. A complex, liquid tissue of d 1.056 and pH 7.35–7.45. It is comprised of erythrocytes (red cells), leucocytes (white cells), platelets, plasma, proteins, and serum. The plasma fraction (55–70%) is whole blood from which the red and white cells and the platelets have been removed by centrifuging. Hemoglobin is a protein found in the erythrocytes. It contains the essential iron atom and functions as the transport agent for oxygen to the heart (artery) and of carbon dioxide from the heart (vein). Experimental work has been reported on the effectiveness of fluorocarbon compounds in carrying out the essential transport functions of blood, especially of the red cells.

Use: Plasma is used to restore liquid volume and thus osmotic pressure in the body where blood loss has been extensive. Animal blood is used as a component of adhesive mixtures. In dried or powder form it is a component of fertilizers poultry feeds and deer repellents.

See also hemoglobin, plasma, platelet, rhesus factor.

bloom. (1) A thin coating of an ingredient of a rubber or plastic mixture that migrates to the surface usually within a few hours after curing or setting. Sulfur bloom in vulcanized rubber products is most common; it is harmless but impairs the eye appeal of the product. Paraffin wax is often included purposely; when it migrates to the surface it provides an efficient barrier to sun-checking and oxidation.

(2) A piece of steel made from an ingot.

(3) An arbitrary scale for rating the strength of gelatin gels. When so used the word is capitalized.

(4) Efflorescence of phytoplankton in sea water causing discoloration of the surface water. See red tide.

blowing agent. A substance incorporated in a mixture for the purpose of producing a foam. One type decomposes when heated to processing temperature to evolve a gas, usually carbon dioxide, which is suspended in small globules in the mixture. Typical blowing agents of this kind are baking powder (bread and cake), sodium bicarbonate or ammonium carbonate (cellular or sponge rubber), halocarbons and methylene chloride in urethane, pentane in expanded polystyrene, hydrazine and related compounds in various types of foamed plastics. Another type is air used at room temperature as a blowing agent for rubber latex; it is introduced mechanically by whipping, after which the latex is coagulated with acid. Air is also used for this purpose in ice cream, whipped cream, and other food products, as well as in blown asphalt and blown vegetable oils.

See also foam.

blow molding. A technique for production of hollow thermoplastic products. It involves placing an extruded tube (parison) of the thermoplastic in a mold and applying sufficient air pressure to the inside of the tube to cause it to take on the conformation of the mold. Polyethylene is usually used but a number of other materials are adaptable to this method, e.g., cellulose, nylons, polypropylene, and polycarbonates. It is an economically efficient process and is especially suitable for production of toys, bottles, and other containers as well as air-conditioning ducts and various industrial items. The method is not limited to hollow products; e.g., housings can be made by blowing a unit and sawing it along the parting line to make two housings.

blown asphalt. See asphalt, blown.

blown oil. (oxidized oil; base oil; thickened oil; polymerized oil). Vegetable and animal oils which have been heated and agitated by a current of air or oxygen. They are partially oxidized, deodorized, and polymerized by the treatment and are increased in density, viscosity and drying power. Common blown oils are castor, linseed, rape, whale and fish oils.

Use: Paints, varnishes, lubricants, and plasticizers.

blue copperas. See copper sulfate.

blue cross gas. See diphenylchloroarsine.

blue gas. See water gas.

blue lead. See lead sulfate, blue basic.

blueprint. See Turnbull's Blue.

blue verdigris. See copper acetate, basic.

blue vitriol. See copper sulfate.

blush. Precipitation of colloidal droplet or lacquer film caused by temperature immediate due to solvent evaporation slightly graying of avoided by use of a

board. See paperboard.

BOD. See biochemical oxygen demand.

body. (1) A non-specific term with connoisseurs descriptive of liquid seed oil which has been used. See also consistency.

(2) In biochemistry, a substance present in the blood. See agglutination.

(3) An object having no color, e.g., blackbody.

Bodroux-Chichibabin reaction. Oxidation of aldehydes to carboxylic acids with Grignard reagents.

Bodroux-reaction. Formation of a color by reaction of a substance with an amino compound by treatment of a substance with a Grignard reagent.

Boeseken's method. A method for determining the configurations of the vicinal groups in vicinal diols by the reduction of the vicinal diols with boric acid for hydroxyl groups on vicinal carbons. Since there is a trans-hydroxyl group it is observed.

Bogert-Cook synthesis. A method for the synthesis of nylons followed by cyclization to form a cyclic polyamide with conformation of octahedral and a small amount of

boghead coal. A variety of coal resembling lignite and behavior durized by a high percentage of volatile matter. Upon distillation high yields of

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13. Thermoplastic Rubbers: A-B-A Block Copolymers

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Thermoplastic rubbers of the A-B-A block copolymer type, where A represents a thermoplastic polystyrene endblock and B represents a rubber midblock of polyisoprene, polybutadiene, or poly(ethylene/butylene), form a useful and versatile group of polymers for pressure sensitive adhesives.

Because of their unique structure, thermoplastic rubbers offer processing advantages to the adhesive manufacturer as well as providing the required performance in a wide range of formulated pressure sensitive adhesive tape and label products. In preparing solvent-based adhesives, thermoplastic rubbers require no premastication, as they dissolve rapidly in common solvents. Thermoplastic rubber adhesives can be coated at much higher solids content than adhesives based on conventional rubbers, because the solution viscosities are much lower. Also, because these rubbers are thermoplastic, they allow preparation of adhesives that can be mixed and coated as solvent-free, hot melt pressure sensitive adhesives.

NATURE OF THE BASIC MOLECULE

Structure

The simplest thermoplastic rubber consists of a rubbery midblock with two plastic polystyrene endblocks. This is pictured schematically in Figure 13-1 where the diamonds represent monomer units in the polystyrene endblocks and the circles represent monomer units in the rubbery midblock. There are two basic classes of the A-B-A block copolymer thermoplastic rubber. One class consists of block polymers in which the rubbery midblock of the molecule is an unsaturated rubber. The two types of polymers in this class are the polysty-

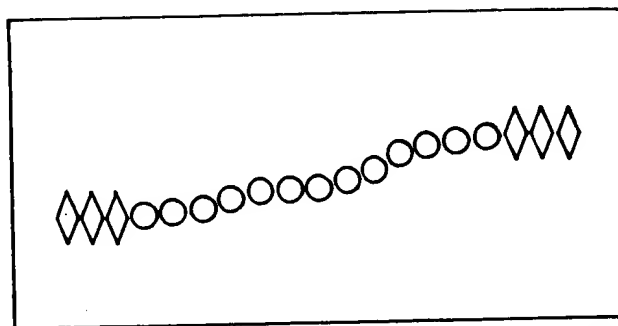
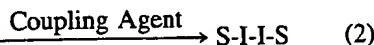
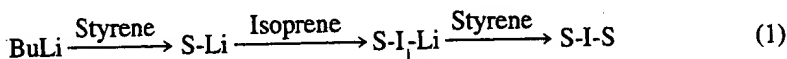


Fig. 13-1. Simplified representation of a thermoplastic rubber molecule.

rene-polybutadiene-polystyrene (S-B-S) polymers and the polystyrene-polyisoprene-polystyrene (S-I-S) polymers. This class of thermoplastic rubber was first marketed commercially in 1965 by the Shell Chemical Company. The second class of thermoplastic rubber consists of block polymers in which the elastomeric midblock is a saturated olefin rubber. The polymers in this class are the polystyrene-poly(ethylene/butylene)-polystyrene (S-EB-S) polymers and the polystyrene-poly(ethylene/propylene)-polystyrene (S-EP-S) polymers. This class of thermoplastic rubber was first marketed commercially in 1972 by the Shell Chemical Company.

The usual method of preparation of thermoplastic rubbers is by anionic polymerization in solvent using an alkyl lithium catalyst such as butyl lithium. S-B-S- and S-I-S-type block polymers may be synthesized by two basic routes, sequential polymerization of all three blocks or sequential polymerization of two blocks, followed by coupling. These two processes are illustrated below, the sequential process in Equation (1) and the coupling process in Equation (2), for the preparation of an S-I-S-type polymer.



The sequential process results in what is called a linear S-I-S polymer. With the coupling process, use of a difunctional coupling agent gives a linear (S-I)₂ polymer, while use of a multifunctional coupling agent gives a multiarmed (S-I)_n polymer. Usual coupling agents are esters or halogen-containing molecules. The literature reports catalytic hydrogenation of S-B-S and S-I-S polymers to produce saturated analogues of the S-EB-S and S-EP-S types, respectively.¹ A

TRADE NAMES

Kraton I
Cariflex
Kraton C
Europrene
Stereon
Tufprene
Finaprene
Solprene

^a Not manufactured

list of the trademarks produced are presented.

Many variations Among these are used in the polymer reaction, and the requirement for glass transition endblocks of a well above room endblocks must. When these are a continuous run idealized representation 13-2.

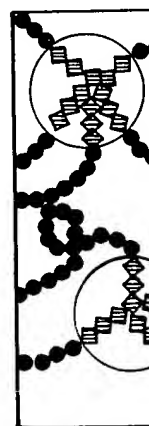


Fig. 1

Table 13-1. Trade Names of Thermoplastic Rubber

TRADE NAME	MANUFACTURER	POLYMER TYPES
Kraton D	Shell	S-B-S, S-I-S, (S-B) _n , (S-I) _n
Cariflex TR ^a	Shell	S-B-S, S-I-S, (S-B) _n
Kraton G	Shell	S-EB-S, S-EP (Diblock)
Europrene SOL T ^a	Enichem	S-B-S, S-I-S
Stereon	Firestone	S-B-S
Tufprene and Asaprene ^a	Asahi	S-B-S
Finaprene ^a	Fina	(S-I) _n
Solprene ^a	Phillips	(S-B) _n

^a Not manufactured in the United States.

list of the trade names, manufactures, and types of thermoplastic polymers produced are presented in Table 13-1.

Many variations can be made in the structure of a thermoplastic rubber. Among these are variations in molecular weight, styrene content, monomers used in the polymerization, the number of polymer arms coupled in the coupling reaction, and the degree of coupling or ratio of (S-I)₂ to (S-I) arms. The key requirement for a thermoplastic rubber is that the rubber midblock, having a glass transition temperature well below room temperature, must have terminal endblocks of a hard, glasslike plastic, having a glass transition temperature well above room temperature. An additional requirement is that the plastic endblocks must be thermodynamically incompatible with the rubber midblock. When these requirements are fulfilled, the polymer can consist of two phases: a continuous rubber phase and a basically discontinuous plastic phase. A highly idealized representation of this phase separated structure is given in Figure 13-2.

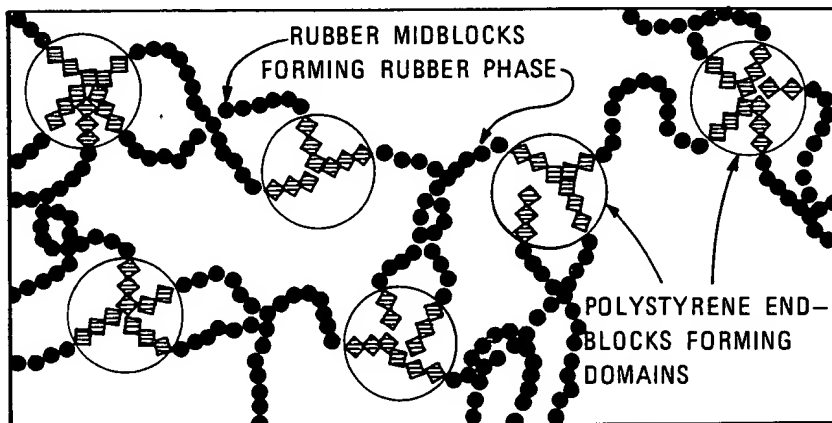


Fig. 13-2. Idealized two-phase network of thermoplastic rubber molecules.

polystyrene-polyisobutylene rubber was first developed by the Goodyear Company. The second class of thermoplastic rubbers is the polystyrene-polyisobutylene copolymers. This class of thermoplastic rubbers was developed by the Shell Chemical Company.

The synthesis of thermoplastic rubbers is by anionic polymerization, such as butyl lithium. There are two basic routes, the linear and the multiarmed, for the polymerization of styrene and isobutylene, as illustrated below, and the process in Equation 13-1.

I-S (1)

t
→ S-I-I-S (2)

I-S polymer. With styrene and isobutylene, it gives a linear (S-I)₂ polymer. With styrene and isobutylene, it gives a multiarmed polymer containing molecules. S-I-S polymers to styrene and isobutylene, respectively.¹ A

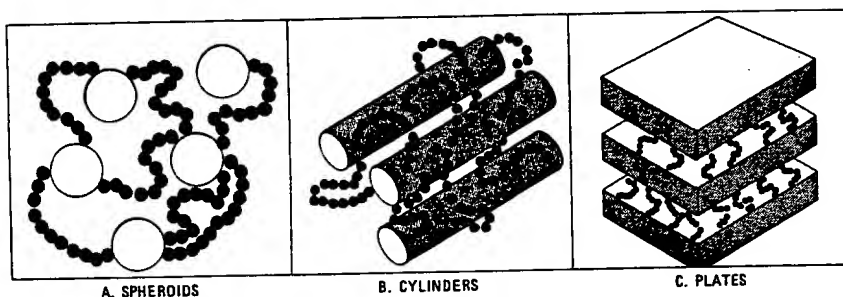


Fig. 13-3. Polystyrene domain configurations or morphologies.

Domains, the plastic endblock phase, are shown in spherical form Figure 13-2. These domains act as cross-links between the ends of many rubber chains, thereby locking the rubber chains and their inherent entanglements in place. This allows the thermoplastic rubber to behave like a conventionally vulcanized rubber that contains dispersed reactive filler particles. However, the thermoplastic rubber is physically cross-linked by the plastic endblock domains rather than being chemically cross-linked like a conventionally vulcanized rubber. These physical cross-link sites (domains) can be reversibly unlocked and reformed by various means, that is, solvation followed by solvent evaporation or through sufficient heating and shearing, then cooling.

The behavior of a thermoplastic rubber is highly dependent on the morphology or geometry of the endblock domains as they are dispersed in the rubber matrix. In commercial thermoplastic rubbers useful for pressure sensitive adhesives, the endblock phase is present in the smaller proportion and is dispersed in a continuous rubber matrix, as suggested by Figure 13-3a, b or c. The uniform dispersion of spherical endblock domains shown in this figure (a, spheroids) is approached only in carefully prepared laboratory samples with low endblock phase concentration. Depending on the endblock phase concentration and on actual processing conditions used to prepare a given sample, the geometry or morphology of the dispersed phase may be spherelike (a), rodlike (b), or lamellar (c) as depicted in Fig. 13-3. The existence of these different morphologies has been confirmed by electron micrographs.^{2,3}

In the latter two cases, the endblock phase may extend as a continuous plastic, rodlike or lamellar, network throughout the rubber matrix. This tends to be the case when the endblock phase concentration is above about 20%w for neat (uncompounded) S-B-S thermoplastic rubbers. In this situation, as the sample is stretched, the initial stress is borne by the plastic network, and the stress-strain properties are greatly affected as discussed below.

Under all conditions the dimensions of the dispersed phase are restricted. Since the junctures between the endblocks and midblocks are located at the phase boundary, the domain thickness is limited to the distance that can be

reached by the endblock sides. For commercial samples, this has been both calculated and measured. For only a small fraction of spheroidal, they do not become transparent, in spite of the two phases. With rodlike morphology, turbidity may exist.

Properties of Neat T

Thermoplastic rubbers are available as porous pellets, or dense pellets, or as sheets. The density of the pellets is about 1.1 kg/m³ (15 lb/ft³) for porous pellets and 1.2 kg/m³ (15 lb/ft³) for pellets. Some pellets are dusting agent, such as talc, which is used on long-term storage of the pellets. The range can vary from 10 to 100 MPa (100 to 1000 psi) depending on polymer and type of rubber.

The hardness and modulus of the rubber depend on the styrene content of the rubber. The styrene content of the rubber is usually between about 10% and 30%w styrene S-EB-S polymer and 30%w styrene S-B-S polymer. The modulus of the polymers show stress-strain curves. However, the soft, 15%w styrene S-B-S polymer has a modulus of 100 MPa (1000 psi), a modulus at break (1400% initial yield point, a tensile strength, 41 MPa (600%). The hardness of the rubbers are generally 10 to 100 MPa (100 to 1000 psi) just described. However, the modulus values as low as 10 MPa (150 psi).

Solution viscosity of the rubbers depends on composition. This behavior is in a solvent such as



morphologies.

used phase are restricted. blocks are located at the the distance that can be

Solution viscosities of thermoplastic rubbers depend strongly on the solvent composition. This behavior will be discussed later in this chapter. However, in a solvent such as toluene, which dissolves both the polystyrene endblocks